

Synthesis, Reactivity, and Properties of New Diaryliodonium Salts as Photoinitiators for the Cationic Polymerization of Epoxy Silicones

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SYNOPSIS

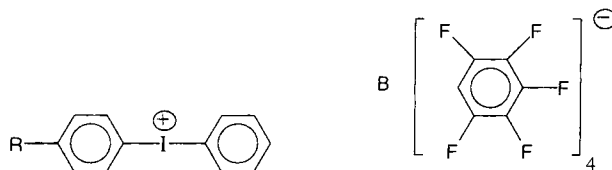
Diaryliodonium tetrakis (pentafluorophenyl) borate salts generate a higher reactivity than any other known diaryliodonium salt. The photochemical properties of diaryliodonium tetrakis (pentafluorophenyl) borate salts were compared to those of the diaryliodonium hexafluoroantimonate salt. The results show that these new salts are the most reactive photoinitiators in this family. In addition, diaryliodonium tetrakis (pentafluorophenyl) borate salts are soluble in low polarity media, such as epoxy silicone oils, which are rich in epoxy groups and insensitive to humidity. These salts have the advantage not to contain a heavy metal (such as antimony). The new properties generated by the use of the tetrakis (pentafluorophenyl) borate anion make the future of the cationic photopolymerization promising. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, special attention has been given to cationic photopolymerization. This technique developed rapidly due to its many advantages:¹ high reactivity, efficiency, and nonpolluting. Cationic photopolymerization is, therefore, a technology used in many fields:² microlithography, the graphic arts, photodoping, release paper, and holography. The most important cationic photoinitiators are the onium salts, especially triarylsulfonium and diaryliodonium salts.³ At the present time, the hexafluoroantimonate anion (A1) exhibits the least nucleophile character.⁴ Accordingly, it is chosen as the counterion of cationic photoinitiators when one wishes to use systems capable of polymerizing rapidly. Using this anion, however, entails two types of problems. Antimony is a toxic heavy metal and brings about problems of recycling when used on a large scale (formation of antimony oxide). On the other hand, the sensitivity of the hexafluoroanti-

monate anion to humidity⁵ poses a problem when this product is stored for a long time. Accordingly, it would really be worthwhile to succeed in replacing hexafluoroantimonate by an anion having a nucleophilic character of the same order, a low toxicity, and exhibiting in regard to humidity.

This challenge was very recently won⁶ (more than 15 years after the discovery of the A1 anion as the counter part of the diaryliodonium cation) by designing new tetrakis (pentafluorophenyl) borate anion (A2), which displays the required properties. Diaryliodonium salts carrying this anion have been prepared.⁶



Their photochemical properties and their reactivity as photoinitiators in a reaction of cationic film polymerization are investigated in the present article.

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EXPERIMENTAL

Reagents

Spectroscopically pure acetonitrile and methanol purchased from Aldrich, as well as dimethoxy phenyl acetophenone (DMPA), sodium 4-nitrophenolate, trifluoromethane sulfonic acid, and cyclohexene oxide were used. 3,4-Epoxy cyclohexylmethyl-3',4'-epoxycyclohexanecarbonate (M01) was supplied by the Ciba Geigy Company (CY179). The epoxysilicone macromer (MS1) has been prepared in a Rhône-Poulenc Laboratory. It is similar to the commercial product UV9300. Bis methyl (trimethylsiloxy) silane was supplied by the Rhône-Poulenc Company. 1,4-Hexadioldiacrylate (HDDA) came from the Société Nationale des Poudres et Explosifs (France). Vinyl hexene oxide was supplied by the Rhône-Poulenc Company and made it possible to prepare bis (trimethylsiloxy) methylethylcyclohexene silane oxide (MS2).

A1 stands for the hexafluoroantimonate anion, A2 for the tetrakis (pentafluorophenyl) borate anion, PI1 for the diphenyliodonium hexafluoroantimonate salt, and PI2 for the diphenyliodonium tetrakis hexafluoroantimonate salt. The cationic parts of the various salts and the anions, except for A2,⁶ are commercially available. The synthesis of A2 is carried out as follows.

Bromopentafluorobenzene (21.3 g, i.e., 0.086 mol) and isopropyl ether were fed, in inert atmosphere, in a 500 mL flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was stirred and cooled to -78°C by using a bath consisting of acetone and carbon dioxide ice.

Hexane solution (52.3 mL of 1.6 M) of *n*-butyllithium (0.97 eq) was fed in the dropping funnel and added within ca 10 min. The mixture was then allowed to stand for 30 min at -78°C with stirring. The dropping funnel was replaced by another one containing 19 mL of a 1.0 M hexane solution of boron trichloride, which was added within 15 min. After being left to stand for 30 min at -78°C with stirring, the reaction mixture was allowed to return to room temperature within ca 1 h. Upon addition of 100 mL of a saturated aqueous KCl solution, the mixture became diphasic and homogeneous. The isopropylether was distilled away. KB (C_6F_5)₄ precipitated towards the end of the distillation, was filtered off, washed with 100 mL of a saturated KCl solution, and vacuum dried at 35°C . A product containing 97% of the expected substance was obtained with a yield of 99%. NMR ¹⁹F $\delta(\text{CDCl}_3)$: -130.2 (sm, 2F); -162.1 (sm, 1F); -165.9 (sm, 1F). NMR

¹³C $\delta(\text{CDCl}_3)$: 125.8 (sm, 1C); 137.7 (dm, 2C, $J_{\text{CF}} = 251.6$ Hz); 139.9 (dm, 2C, $J_{\text{CF}} = 251.6$ Hz); 149.6 (dm, 1C, $J_{\text{CF}} = 251.6$ Hz). UV (CH_3OH) $\lambda_{\text{max}}(\epsilon)$: 225 (4730). IR (cm^{-1}): 1645.5m (penta subst. benz.); 1515.5s (penta subst. benz.); 1278.0m (penta subst. benz.); 1090.2vs ($\text{C}_{\text{aro-F}}$); 1032.1w; 979.8s; 775.2m; 756.9m; 684.1m; 660.3m (B-C). 7.17 g (i.e., 22.6 mol) of diphenyliodonium chloride was dissolved in 300 mL of water contained by a 1000 mL Erlenmeyer flask; 15.52 g (i.e., 22.6 mol) of lithium tetrakis (pentafluorophenyl) borate dissolved in 250 mL of water was added dropwise. The mixture was left to stand for 30 min with stirring and then filtered. The filtrate was vacuum dried (133 Pa) for 1 night, away from the light. Diphenyliodonium tetrakis (pentafluorophenyl) borate (16.33 g) was, thus, recovered (with a yield of 75%). NMR ¹⁹F $\delta(\text{CDCl}_3)$: -130.2 (sm, 2F); -162.1 (sm, 1F); -165.9 (sm, 1F). NMR ¹H $\delta(\text{CD}_3\text{OD})$: 7.52 (tm, 4H_{aro}, $J_3 = 7.2$ Hz); 7.65 (tm, 2H_{aro}, $J_3 = 7.2$ Hz); 8.16 (dm, 4H_{aro}, $J_3 = 7.2$ Hz). UV (CH_3OH) $\lambda_{\text{max}}(\epsilon)$: 227 (17800). IR (cm^{-1}): 1644.5m (penta subst. benz.); 1514.9s (penta subst. benz.); 1462.8vs (mono subst. benz.); 1276.1m (penta subst. benz.); 1086.1s ($\text{C}_{\text{aro-F}}$); 979.2s; 775.1m; 683.9m; 661.5m (B-C); 645.0w; 605.9w.

Conventional Spectroscopies

The UV/Vis spectra were recorded on a Beckman DU7 apparatus and the IR spectra on a Perkin-Elmer 1600 series FTIR appliance.

RTIR Spectroscopy

The method used for the real-time investigation of the kinetics of polymerization consisted of simultaneously exposing the sample to a UV illumination that initiated the polymerization, and to an IR illumination that made it possible to follow the disappearance of a functional group.⁷ Let C_i be the conversion ratio at time t_i and $[\text{M}]_0$ the concentration of the monomer at time t_0 . It follows therefore:

$$R_p = \frac{C_2 - C_1}{t_2 - t_1} \times \frac{[\text{M}]_0}{100}$$

Gas Chromatography (GCMS)

The samples were investigated through GCMS on a Hewlett Packard 5971 Series apparatus. A capillary column of type SE 30 was used.

Illumination Techniques

The illuminations were carried out by starting from two lamp types, either with a mercury vapour lamp (HPK 125 W) or by using a UV lamp fitted with a conveyor of model IST (lamp UV 200). The incident intensities were measured with a radiometer (International Light).

Determining the Residual Acidity

The quantity of residual acid was determined according to a method of analysis developed by Gaines.⁸ This very sensitive method allows the determination of acid quantities in the order of 10^{-9} mol. In addition, it is safer to use a nonaqueous method, to avoid hydrolysis of the salts. For instance, hydrolysis of the hexafluoroantimonate produces hydrofluoric acid makes a precise determination of the acid difficult.⁹ S. A. McDonald¹⁰ described the use of merocyanine as a nonaqueous system that is suitable for the determination of the concentration of Brönsted acid. Merocyanine becomes protonated under the effect of a strong acid. The protonated species exhibits an absorption band that is not available in the dyestuff. The concentrations of acid can be determined in acetonitrile or dichloromethane by following the O.D. of this absorption band after standardizing with a strong acid. According to the same principle of determination, J. L. Dektar and N. P. Hacker¹¹ used sodium 4-nitrophenolate instead of merocyanine. The equilibrium described in Figure 1 depends on the acidic strength. The precision of the determination of the acid concentration is, therefore, dependent on the shift of equilibrium to the formation of 4-nitrophenol. A standardization was performed, in order to find out the relationship between the equilibrium and the acidic strength. Known quantities of trifluoromethane sulfonic acid were added to a sodium nitrophenolate solution and the spectrum of visible absorption was recorded (Fig. 2). A linear correlation was observed between the added acid equivalent and the disappearance of the band at 427 nm. Compositions having a concentration of iodonium salt of 10^{-5} mol/g were investigated. The illumination was carried out by using a UV lamp fitted with a conveyor. The quantity of acid was determined before and after illumination; the difference between these two values gave the quantity of residual acid in the film. Each analysis was performed on four samples and the average of the obtained results was taken into account. The average error is less than 10%. A solution of dyestuff was prepared by dis-

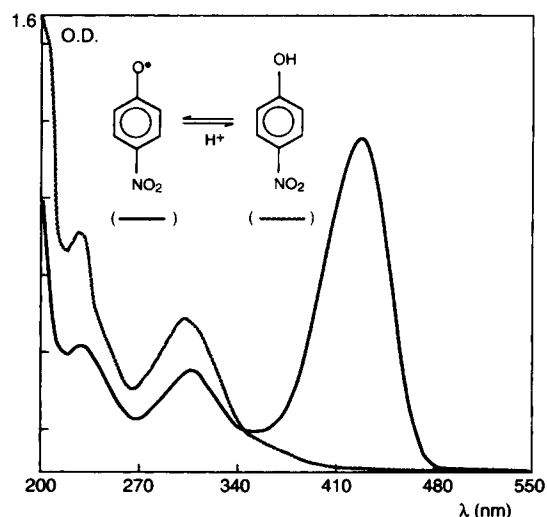


Figure 1 Absorption spectrum of sodium 4-nitrophenolate and 4-nitrophenol in acetonitrile.

solving sodium *p*-nitrophenoxide in 100 mL of spectroscopically pure acetonitrile and then by diluting down to an O.D. of 1.8 at $\lambda = 427$ nm. Polymer films having a thickness of 36 microns, obtained from a calibrated bar and spread on a glass plate, were dissolved in 5 mL of dyestuff solution. The obtained solution was subjected to an ultrasonic treatment for half an hour and the acidity was then determined.

RESULTS AND DISCUSSION

Effect of Anion Nature on the Photochemical Reactivity of Various Photoinitiators

The reactivity of cationic photoinitiators carrying various anions was tested in organic and silicone medium. This study was carried out under real conditions (a UV lamp fitted with a conveyor was used). The polymerization was performed on glassine. The results achieved with the photoinitiators PI1, PI12, PI13, and PI14 that were fitted with anion A1, demonstrate unambiguously that diaryliodonium salts have the same order of reactivity, and they are much more reactive than ferrocenium salts. It should be noted that the order of reactivity for the anions is as follows (cf. Table I): $B(\phi F_5)_4^- > SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$. In these experiments of film polymerization with various photoinitiators, the diphenyliodonium tetrakis (pentafluorophenyl) borate salt (PI2) displayed a reactivity of the same order as its hexafluoroantimonate homologue (PI1) in organic media (M01) and proved more effective in silicone medium (MS1). The reactivity of photoinitiator PI2 is substantially higher than that of other

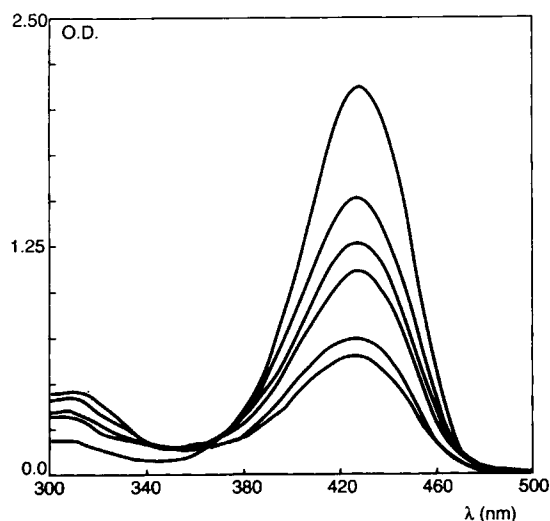


Figure 2 Disappearance of the absorption band at 427 nm of sodium 4-nitrophenolate when known quantities of trifluorosulfonic acid were added.

commercially available cationic photoinitiators PI4, PI3, and PI14. Semiindustrial testing (1 Fusion lamp H) revealed that photoinitiator PI2 allows curing speeds higher than 200 m/min to be attained, whereas under the same conditions one can only proceed at 100 m/min with PI1, PI3, PI4, or PI14.¹³

Kinetics of Polymerization

The rate constant of the propagation step is directly related to the nature of the ion pair formed by the active species and the counterion. The wider the components of the ion pair stand apart (are free), the higher will be the rate of the propagation step.

Consider that the polymerization takes place according to a conventional scheme where an initiation, a propagation, a termination, and a transfer reaction are successively involved.¹ In this case, active centers are formed through various mechanisms and remain active until they are destroyed by a termination reaction. The rate of the initiation step is defined as:

$$Ri = k_i [H^P] \cdot [M]$$

$$\text{i.e., } Ri = k_i \Phi_i I_a \cdot [M]$$

where $[M]$: stands for the concentration of monomer Φ_i : for the quantum yield of acid formation, and I_a : for the absorbed light intensity.

If a stationary state becomes established, the appearance rate of the cation centers equals, then their disappearance rate, hence:

$$k_i [H^P] \cdot [M] = k_t \cdot [C^P]$$

$$\text{hence, } [C^P] = k_i [H^P] \cdot [M] / k_t,$$

$$\text{i.e., } [C^P] = k_i \cdot \Phi_i \cdot I_a \cdot [M] / k_t$$

The rate of polymerization is defined as:

$$R_p = d[M]/dt = k_p [M] \cdot [C^P]$$

The degree of polymerization is expressed as:

$$DPn = (dM/dt) / (dN/dt)$$

$$= k_p [M] \cdot [C^P] / (k_{tr(m)} \cdot [M] \cdot [C^P] + k_s [C^P] + k_t [C^P] + k_{tr(s)} \cdot [S] \cdot [C^P]).$$

R_p and DPn can be considered as proportional to k_p if the counter anion has no effect on the rate of initiation: this assumption seems to be valid because the photolysis, the acidity measurements, the GCMS experiments show no substantial difference when using anion A1 or A2. Other works on the effects of the anion reach to the same conclusions.³

Polymerization Kinetics of Monomer M01

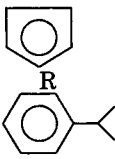
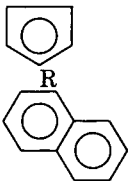
Monomer M01 was used in this study. Since it contains two epoxy groups, a three-dimensional network was formed when polymerization took place. The resin was applied as a 15 mm thin layer on a polypropylene film. The IR spectrophotometer was adjusted at the detection wavelength corresponding to the maximum absorption of the stretching band of the epoxy function, i.e., 790 cm^{-1} . The photosensitive mixture contained 10^{-2} mol/L of photoinitiator. A maximum rate of $R_p(A2) = 0.26 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ was found for system (M01/PI2) [Fig. 3(a)]. For system (M01/PI1), it only attains: $R_p(A1) = 0.12 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. One can write:

$$R_p(A1) / R_p(A2)$$

$$= k_p(A1) / k_p(A2), \text{ i.e., } k_p(A2) = 2.2 k_p(A1).$$

It is, therefore, apparent that, in organic medium, the propagation rate of anion A2 is ca twice higher than that of anion A1. It is also worthy of note that the conversion ratio varies from system to system: 50% for PI2 and 30% for PI1. These low conversion ratios can be attributed to a quick solidification of the sample, that prevents diffusion of the residual monomer.

Table I Effect of Nature of Anion on the Various Cationic Photoinitiators

| Ref. | Photoinitiators | | Conc. $\times 10^{-3}M$ | Mass % | M01 | | MS1 | |
|------------------|--|----------------------------------|----------------------------|--------|----------|--------------|----------|--------------|
| | Cation | Anion | | | <i>N</i> | V (m/min) | <i>N</i> | V (m/min) |
| PI1 | Ph ₂ I | SbF ₆ | 20 | 1 | 1 | > 60 | 2 | > 30 |
| PI2 | Ph ₂ I | B(ΦF ₅) ₄ | 6 | 0.5 | 1 | > 60 | 1 | > 60 |
| PI3 | Ph—I—Ph—OC ₈ H ₁₇ | SbF ₆ | 20 | 1.2 | 1 | > 60 | 2 | > 30 |
| PI4 UV9310C | (Ph—C ₁₂ H ₂₅) ₂ I | SbF ₆ | | 3 | 1 | > 60 | 1 | > 60 |
| PI4 UV9310C | (Ph—C ₁₂ H ₂₅) ₂ I | SbF ₆ | | 1 | 3 | > 20 | 8 | > 7 |
| PI5 | Ph ₂ I | AsF ₆ | 20 | 0.9 | 3 | > 20 | 8 | > 7 |
| PI6 | Ph ₂ I | PF ₆ | 20 | 0.8 | 4 | > 15 | 8 | > 7 |
| PI7 | Ph ₂ I | BF ₄ | 20 | 0.7 | 10 | > 6 | 15 | > 4 |
| PI12 STE 1 |  | SbF ₆ | 20 | 1 | 10 | > 6 | 14 | > 4 |
| PI13 STE 2 |  | SbF ₆ | 20 | 0.8 | 5 | > 12 | 9 | > 6 |
| PI14 Cyracure | Φ ₃ S | SbF ₆ | | 3 | 1 | > 60 | 1 | > 60 |
| PI15 | Φ ₃ I | PF ₆ | 20 | 0.8 | 3 | > 15 | 8 | > 7 |

The cationic part is commercially available. Anions are exchanged. Problems with solubility of the photoinitiators are known except for PI2. A carrier solvent can be used to improve the solubility. Accordingly, the indicated concentrations can be considered as maximum values. Whatever these problems, it is perfectly clear that PI2, PI4, PI14, and PI1, PI3 are the best photoinitiators.

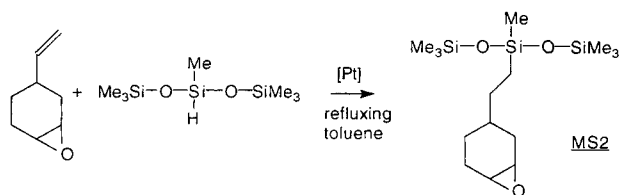
N: Number of passings under UV lamp fitted with conveyor, that are required to produced a crosslinked (nonsticky) film.

V: Permitted speed of curing.

Illumination energy in 1 passing: 54 mJ/cm².

Polymerization Kinetics of an Epoxy Silicone Monomer

Since the IR band of the epoxy function of monomer MS1 is overlain by that of the siloxane functions, it was not possible to follow the crosslinking kinetics of this monomer. An epoxy silicone monomer (MS2) having a higher epoxy/siloxane ratio was prepared through the following hydrosilylation reaction:



The disappearance kinetics of the epoxy function of this monomer can be followed at 787 cm⁻¹. It was found that for system (MS2/PI2), the maximum rate is [Fig. 3(b)]: $R_p(A2) = 0.72 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. For system (MS2/PI1), it only attains: $R_p(I) = 0.29 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. By using the formula $R_p = k_p[M][CP]$ and for the same conversion ratio, one can write:

$$\begin{aligned} R_p(A1)/R_p(A2) \\ = k_p(A1)/k_p(A2), \text{ i.e., } k_p(A2) = 2.5 k_p(A1) \end{aligned}$$

It is also worthy of note that the conversion ratio varies from system to system: 75% for PI2 and 60% for PI1. In silicone medium, the constant of the

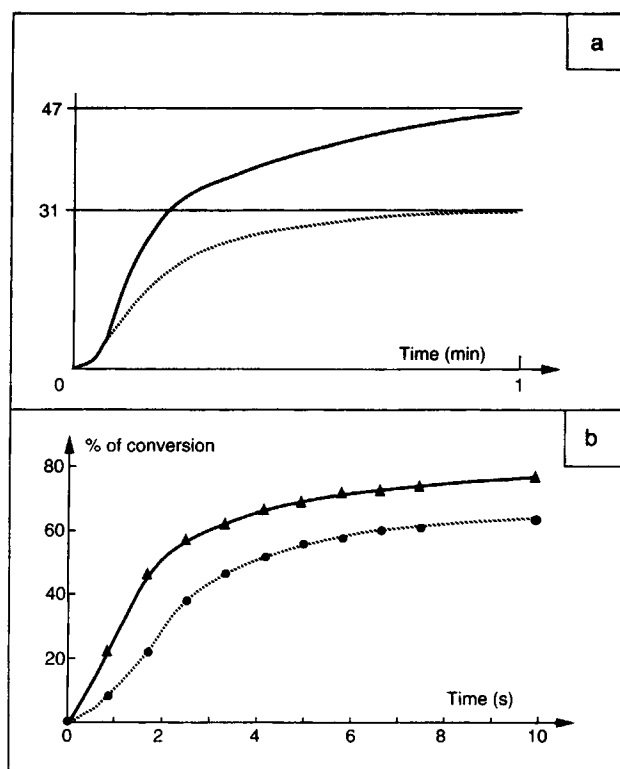


Figure 3 Polymerization profiles obtained with the photoinitiators PI1 (· · · · ·) and PI2 (—) at a concentration of 10^{-2} mol/L in 15 mm thick films on a polypropylene substrate. (a) In the presence of monomer M01. (b) In the presence of monomer MS2.

propagation rate of anion (A2) is 2.5 times higher than that of anion (A1).

Evaluating the Ratio of the Propagation Rates $k_p(A2)/k_p(A1)$ Relevant to the Anions (A1) and (A2) through the Determination of M_n

In order to compare the k_p values obtained (through the evaluation of M_n) when the anions (A1) and (A2) were used, one must proceed under well-defined conditions. First of all, this study was confined to the polymerization of a monofunctional monomer that produces linear polymer chains whose degree of polymerization (DPn) can be determined experimentally. Determining the DPn implies dissolving the obtained chains in THF or butylacetate. This can be done for the cyclohexene polyoxide that is soluble in THF, but is not possible for the polymer prepared from monomer MS2 that is insoluble in both solvents. Accordingly, this study was carried out with cyclohexene oxide (MO2). The polymerization was conducted in a solvent/monomer mixture with a mass ratio of 50 : 50. Toluene, whose

transfer constant $k_{tr(s)}$ is negligible, was used as a solvent. The concentration of photoinitiator was fixed at a low value (2.61×10^{-7} mol per g of reaction mixture), to keep the polymerization under control (highly exothermic reaction). The illumination was carried out by using a convection cooled mercury vapor lamp of type HPK 125 W delivering a power of 2.73 mW/cm^2 to the reaction medium. It is well-known that the degree of polymerization can be written as:

$$DPn = \frac{k_p[M] \cdot [C^P]}{(k_{tr(m)} \cdot [M] \cdot [C^P] + k_s[C^P] + k_t[C^P] + k_{tr(s)} \cdot [S] \cdot [C^P])k_{tr(s)} \cdot [S] \cdot [C^P]}$$

can be left out in the present case.

Put $K_t = k_s + k_t$. DPn may be written as:

$$DPn = \frac{k_p[M]}{(k_{tr(m)}[M] + K_t)}$$

Then, on the assumption $k_s + k_t \ll k_{tr(m)}[M]$, one may write: $DPn = k_p/k_{tr(m)}$. If one considers that the constant of transfer to the monomer $k_{tr(m)}$ is mainly dependent upon the nature of the monomer, by measuring the DPn values obtained according to whether anion (A1) or anion (A2) is used, the following equation holds: $k_p(A1)/k_p(A2) = DPn(A1)/DPn(A2)$ or still: $k_p(A1)/k_p(A2) = M_n(A1)/M_n(A2)$. Gel permeation chromatography (GPC) made it possible to measure the M_n of the various polymers obtained with the photoinitiators PI1 and PI2. The M_n of the obtained polymer was estimated at $M_n(A1) = 2050$ when using anion (A1) and $M_n(A2) = 4145$ in the case of anion (A2). It may be inferred, therefore, that the ratio of the constants of the propagation rates when the anions (A1) and (A2) were used is $k_p(A1)/k_p(A2) = 2050/4145 = 0.49$. That is to say, with anion (A2) the propagation reaction took place twice as quick as with anion (A1): $k_p(A2) \sim 2 \cdot k_p(A1)$.

Mechanism of Photolysis

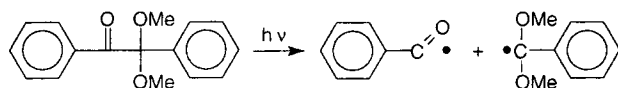
In view of the very favourable reactivity of photoinitiator PI2, the researchers wanted to find out whether the mechanism of its photolysis is identical or whether it differs from that of conventional iodonium salts. In order to answer this question, several aspects of the photolysis of iodonium salts were investigated. First of all, the kinetics of polymerization of acrylate systems were compared, in order to find out whether the numbers of radicals generated in the photolysis of the iodonium salts PI1 and PI2 are identical. The second investigation was concerned with the changes of the UV spectra of the

products formed during the illumination. The third one dealt with the quantity of acid that was formed, while the fourth approach was aimed at the nature of the photolysis products.

Investigating the Mechanism of Radical Formation

Formulations having a photoinitiator concentration of 2×10^{-2} mol/L were prepared. Regarding the photoinitiators, the salts PI1 and PI2 were used and, by way of comparison, DMPA, which is a conventional radical photoinitiator. Regarding the acrylates, a 50 : 50 mixture of a multifunctional epoxy acrylate oligomer and HDDA was used. HDDA was introduced in the formula to provide some flexibility and, thus, to produce homogeneous films in the polymerization. The various formulations were applied on KBr pellets. The disappearance of the band that characterizes acrylates (1630 cm^{-1}) was followed by using FTIR [Fig. 4(a)]. This provided a means for determining the percentage of conversion in the irradiation [Fig. 4(b)]. The highest conversion (60%) was achieved with dimethoxyphenylacetophenone, DMPA (Irgacure 651 from Ciba). This was an expected result, because DMPA is a radical photoinitiator, which, under the effect of UV light, produces radicals capable of initiating the polymerization according to a NORRISH 1 mechanism of α -cleavage.

NORRISH 1 reaction



The conversions obtained with the photoinitiators PI1 and PI2 are in the same order of magnitude: 29 and 25%, respectively. Hence, it follows that illumination of salt PI2 practically produces the same number of radicals as that of salt PI1. The hypothesis of an additional production of radicals by anion (A2) should, therefore, be ruled out and it may be inferred, therefore, that the photochemistry of salt PI2 should occur mainly through the conventional mechanism of the diphenyliodonium salt³ (the number of radicals generated appear to be the same for both photoinitiators).

Changes of the UV Spectra during Photolysis in Solvent Medium

The changes of the UV spectra were followed during photolysis in the acetonitrile and the methanol of 3.5×10^{-4} mol/L iodonium salt solutions. The il-

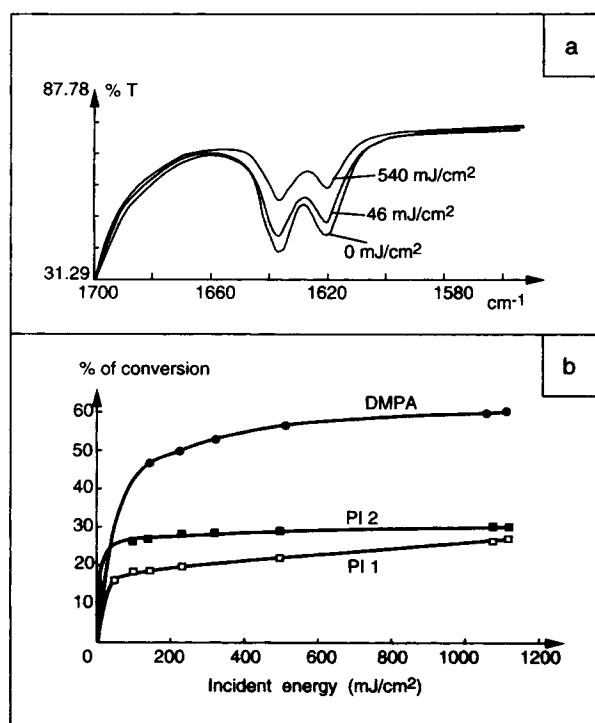


Figure 4 Disappearance kinetics of the acrylate function. (a) Disappearance of the acrylate band at 1630 cm^{-1} on UV illumination. Photoinitiator: DMPA $c = 2 \times 10^{-2}$ mol/L. (b) Changes in the conversion of the acrylate function for various photoinitiators.

lumination was conducted by using a convection cooled HPK 125 W lamp. The results obtained for the salts PI2 and PI1 are entirely identical; the UV spectra recorded throughout the photolysis display the same shape. Accordingly, the same products were formed on illumination of the salts PI1 and PI2. One observed a difference in the changes of the UV spectra according to whether the experiments were performed in acetonitrile or methanol. In acetonitrile, the optical density increased over the whole range of the spectrum throughout the photolysis, while the wavelength of the maximum absorption shifted from 237 to 227 nm [Fig. 5(a)]. In methanol, several absorption bands emerged at 289 and 358 nm during the first 30 min. Later on, these bands disappeared gradually, so that ultimately a spectrum exhibiting a maximum absorption at 229 nm was obtained [Fig. 5(b)]. This spectrum was comparable to that obtained on photolysis in acetonitrile. Under the effect of UV light, the photoproducts that had been formed generated second generation photoproducts. Photolysis of the photoinitiators PI2 and PI1 generated the same photoproducts. The mechanisms of photolysis of these salts in protic solvents and in acetonitrile seem, therefore, to be identical.

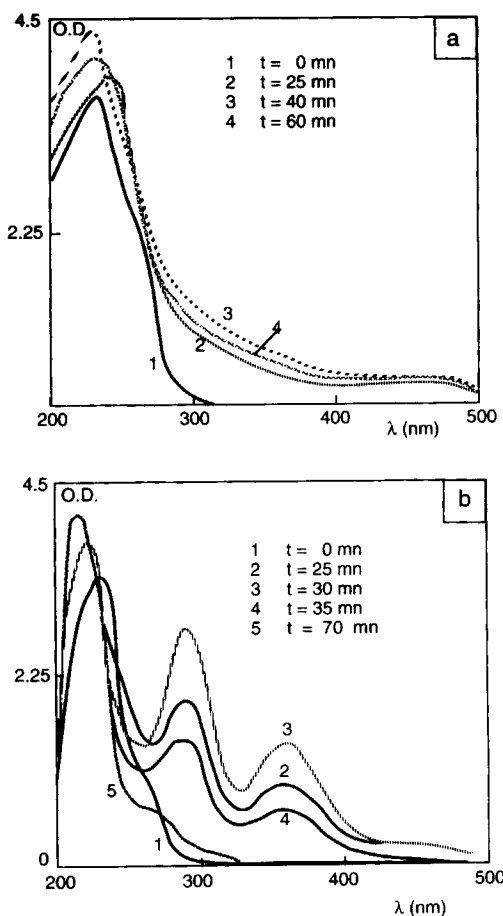


Figure 5 Changes in the UV spectrum during the photolysis of PI1 and PI2. (a) In acetonitrile. (b) In methanol.

Investigating Acidity Changes in Films

This study was conducted with the monomers M01 and MS1. After checking for the absence of acid in these monomers, the quantity of acid was determined in films obtained by using different illumination energies and the photoinitiators PI1 and PI2. These quantities of acid do not correspond to the concentration of the acid species during the polymerization step: they must be considered as the residual acidities present in the film after the curing process (so, they cannot infer the hypothesis of a stationary state). The results are shown in Table II. The residual acidities are the same with the salts PI1 and PI2. A film obtained after one passing at a speed of 60 m/min under the UV lamp, i.e., with an energy of 45 mJ/cm², contained 3×10^{-6} mol of acid per gram of film, while a film produced after two passings at a speed of 5/min, i.e., with an energy of 1080 mJ/cm², contained 11×10^{-6} mol of acid per gram. Bearing in mind that after two passings at a speed of 5 m/min no iodonium salt is left in the

film, it can be concluded that 1.04 mol of iodonium salt produces at least 1.10 mol of acid, i.e., the ratio R defined as: quantity of acid that was found over quantity of photolyzed salt, equals $106 \pm 10\%$. The values determined for the photoinitiators PI1 and PI2 were identical both in the organic and the silicone matrix. Hacker¹² reported the formation of 5.50 mol of acid for 5.33 mol of consumed iodonium salt, i.e., $R' = 102\%$ for the photolysis of 10^{-2} mol/L iodonium solutions in acetonitrile.

Nature of Photolysis Products

The 10^{-2} mol/L solutions of the salts PI1 and PI2 in acetonitrile were photolyzed and then analyzed by using GCMS. It can be seen from Figure 6(a) and (b) that the photolysis products are identical, apart from a product emerging after a retention time of 12 min and 13 s, whose spectrogram did not allow its identification. This product, however, is not predominant and accounts only for a minor percentage of the photolysis products. The other photolysis products were identified by MS: iodobenzene (time: ≈ 6.4 mn), biphenyl (time: ≈ 17.8 mn), and iodobiphenyl (time: ≈ 26.3 mn). Integration of the peaks of the chromatograms makes it possible to conclude that they were formed in the same proportions for both salts and, therefore, most certainly according to the same mechanism. Evidence was provided for the stability of acid HB (C₆F₅)₄. The NMR spectrum of the ¹⁹F of anion A2 remained unchanged on completion of the photolysis of salt PI2.

CONCLUSION

Diaryliodonium tetrakis (pentafluorophenyl) borate salts are more reactive than diaryliodonium hexafluoro-

Table II Determining the Quantity of Acid Found in Different 36 Micron Thick Polymer Films

| Monomer | Photoinitiator | Irradiation Energy mJ/cm ² | Residual H ⁺ 10 ⁻⁶ mol/g of film |
|---------|----------------|---------------------------------------|--|
| MS1 | PI2 | 45 | 3 |
| | | 1080 | 11 |
| | PI1 | 45 | 3 |
| | | 1080 | 11 |
| MO1 | PI2 | 45 | 3 |
| | | 1080 | 11 |
| | PI1 | 45 | 3 |
| | | 1080 | 11 |

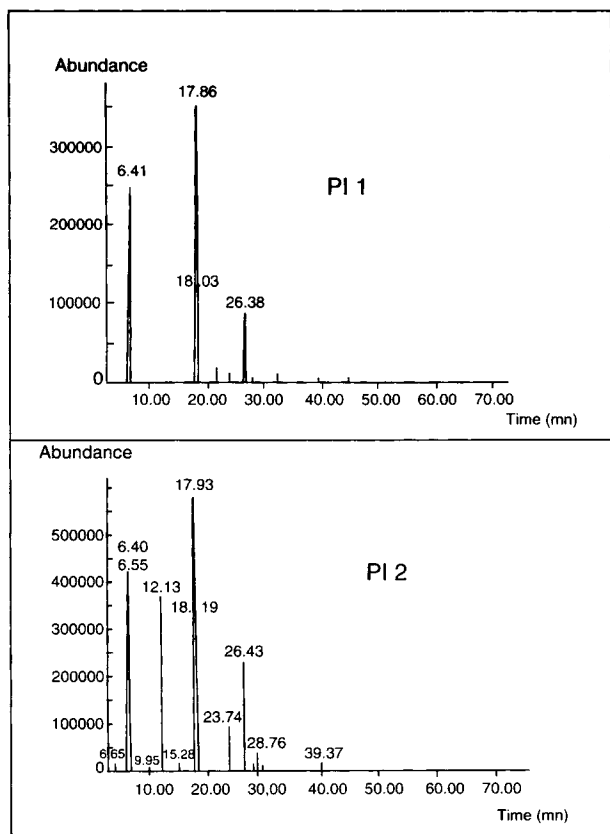


Figure 6 Chromatogram of the photolysis products of PI1 and PI2.

roantimonate salts. Accordingly, they make it possible to attain higher curing speeds. This higher reactivity can be accounted for by the higher propagation rate constants concerned with these anions. The mechanism of photolysis of the diphenyliodonium tetrakis (pentafluorophenyl) borate salts is identical to that of conventional iodonium salts. Indeed, the same distribution and nature of the photolysis products, the same number of generated radicals, and the same amount of residual acid are observed. In addition, the insensitiveness of the tetrakis (pentafluorophenyl) borate anion to humidity imparts a several day pot life in an epoxy silicone. When hexafluoroantimonate salts are used, this period is less than 1 day. Moreover, the problem related to the formation of antimony oxide no longer claims attention. Results on an industrial scale were reported recently.¹³

This new cationic photoinitiator seems very promising for the photopolymerization of epoxy

modified silicones: higher reactivity, higher solubility, less toxicity.

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